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Report USNA-EPRD-39

POLAROGRAPHY OF ORDNANCE COMPOUNDS

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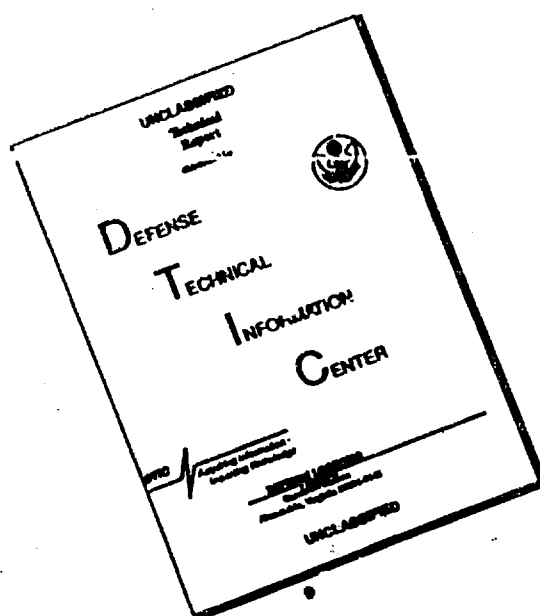
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Preliminary investigation indicates that Single Sweep Polarography is capable of distinguishing between and measuring concentrations of various ordnance compounds present in low concentrations in water solution without resorting to extractions or mixed solvent systems.		

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INTRODUCTION

As pointed out in an interim report (USNA-EPRD-17), it is highly desirable to have available quick and continuous monitoring methods so that waste streams from production and/or washing plants may be analyzed for various ordnance compounds. In addition, it is also necessary to follow and know the status of various degradation techniques used for these same compounds. Some of the compounds of interest are RDX, TNT, HMX, Otto Fuel, and nitramines in general. Colorimetric, Gas Chromatographic, Atomic Absorption and other methods have been tried, but Dr. Gerald Whitnack of the Naval Weapons Center has felt that polarography should be considered and has suggested that additional information on polarographic methods be obtained. Thus, this work represents an attempt to add to the body of knowledge available on the polarographic behaviour of ordnance compounds when present in solution in low concentrations. Polarographic determination of nitroglycerin in Double-Base Powder has been studied, but the method involves an alcoholic extraction and the subsequent measurement is made in a 75% alcohol solution.¹ Nitro and Nitrosoguanidine have been measured at the dropping mercury electrode.² The determination of TNT by Linear Sweep Polarography as done by Whitnack is the forerunner of the present study, but it must be noted that this work was done in 25% acetone solution.³ The determination of PGDN (a component of OTTO Fuel) has also been done polarographically, but only after extraction and then in an electrolyte that contains ethyl alcohol.^{4,5,6} These examples point out the need to obtain data on polarographic behaviour of ordnance compounds, but in aqueous solutions only as opposed to mixed solvent systems. Since it is desirable to measure ordnance compounds in waste streams, it is hopeful that measurements may be more direct and that mixed solvent systems will not have to be employed.

¹Whitnack, Gerald C., Margaret M. Mayfield, and E. St. Clair Gantz, Analytical Chemistry 27, 899 (1955)

²Whitnack, Gerald C. and E. St. Clair Gantz, Journal of the Electrochemical Society 106, 422 (1959).

³Whitnack, Gerald C., Analytical Chemistry 35, 970 (1963).

⁴Gogis, William A. and Jerry D. Hamrick, U.S. Naval Propellant Plant, Indian Head, Maryland: "The Polarographic Determination of 1, 2 Dinitroxypropane."

⁵Cox, Walter G., NUSC Newport, R.I., TM No. SB322-4546-72: "The Polarographic Investigation of Organic Nitrate Esters I, The Electroanalytical Determination of Propylene Glycol Dinitrate."

⁶Cox, Walter G., S. Milligan and H. Peter Hirschler, NUSC Technical Report 4420 of 14 June 1973. "Otto fuel II: Evaporation into Air and Diffusion into Sea Water."

EXPERIMENTAL

All measurements for this problem were made using a PAR Model 170 Electrochemistry System. The electrode used was a hanging mercury drop of various sizes in order to change the sensitivity. The technique involved a rapid single sweep of the potential range with a new hanging mercury drop provided for every sweep. Measurements were made vs. the Standard Calomel Electrode and all potentials reported are volts vs. SCE. The electrolyte was varied as was the sweep rate and the potential range studied.

Peak potentials measured by this method are related to reduction potentials for reversible systems but normally bear no simple relationship to reduction potentials for irreversible systems. The reductions carried out during this study are irreversible and thus this complication is one of importance. It is expected, however, that the current at the peak potential will be proportional to the concentration of the species being reduced and thus the method does have application in measurements of concentration even though the electrochemistry involved is complicated and may not give direct information concerning the nature of the active material.

The solutions used were saturated solutions (less than 50 ppm) of RDX and HMX. Both RDX and HMX are nitramines. Before reduction, the solutions were flushed with nitrogen gas to remove dissolved oxygen and the measurements were made in still solutions to insure that mass transfer was a result of diffusion only. Even though the electrolyte was varied, as discussed in the results section, only aqueous media were employed.

A single measurement was obtained by introducing an aliquot of the saturated solution (RDX or HMX) to be studied into a suitable electrolyte, the system flushed with nitrogen for fifteen minutes and after the solution was allowed to become still, a drop of mercury on the end of a capillary tube was introduced into the solution. A standard saturated calomel electrode was used as the reference and a piece of platinum wire as the current carrying electrode. This arrangement permits those potentials measured to be independent of the current, although the current carried at any one potential is related to concentration of active species. Sensitivity was varied both electronically using the options provided on the instrument, or by changing the size of the mercury drop. Potential ranges were chosen simply on the basis of where the reductions were taking place within the overall potential

range of -0.1 to -1.5. Beyond these limits other complications arise which do not allow the technique to be useful.

The change in sweep rate does effect the peak potentials and currents measured since the reductions under investigation are irreversible and thus the rate of diffusion may or may not control a particular measurement. When care is taken to reproduce the solution concentration, mercury drop size, and other parameters such as sweep rate, etc., reproducibility is very good and no further comment on this point is made.

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RESULTS

Supporting Electrolyte

Measurements on RDX and HMX in both 0.5 M KCl and 0.1 M acetate buffer (0.05 M each in acetic acid and sodium acetate) indicate that the reduction waves obtained are independent of which electrolyte is chosen. The pH of the KCl solution was 5.5 while the pH of the acetate buffer was 4.6. Qualitative determinations of effect of pH by making measurements after additions of small quantities of acid or base indicate that within this pH range, no pH dependence is noted. All of the remaining measurements were made in 0.5 M KCl for convenience but it should be pointed out that it may be necessary to employ a buffer in actual applications since the pH of the source being tested may change markedly from sample to sample. Neither the acetate buffer taken alone nor the KCl solution taken alone (at adjusted pH's of 2.5 to 11.0) show any reductions in the potential ranges scanned in this study.

Dissolved Oxygen

It was determined that flushing with nitrogen before polarographs were obtained was a necessity, as expected. Reduction waves appeared in the range of -0.1 to -0.2 and in the range of -1.0 to -1.2 volts when the supporting electrolytes were run alone and before oxygen was removed (see Figure 1). No attempt was made to identify these reduction waves and all subsequent analyses were performed only after a minimum of 15 minutes of N_2 flushing of the solution. In addition, a flow of N_2 gas was maintained over the surface of the solutions being analyzed in order to prevent any diffusion of O_2 back into the solution.

Current 5 μ A Full Scale

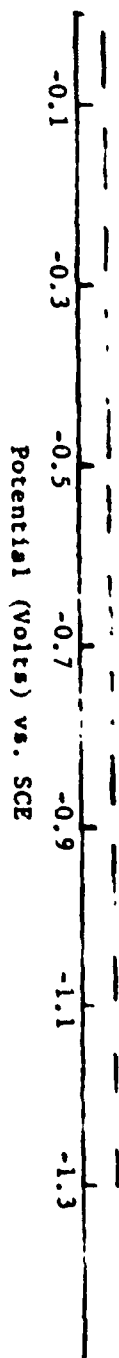


Figure 1
0.5 M KCl vs. SCE
Sweep Rate 200mV/sec
Before N₂ flushing
After N₂ flushing (15 minutes)

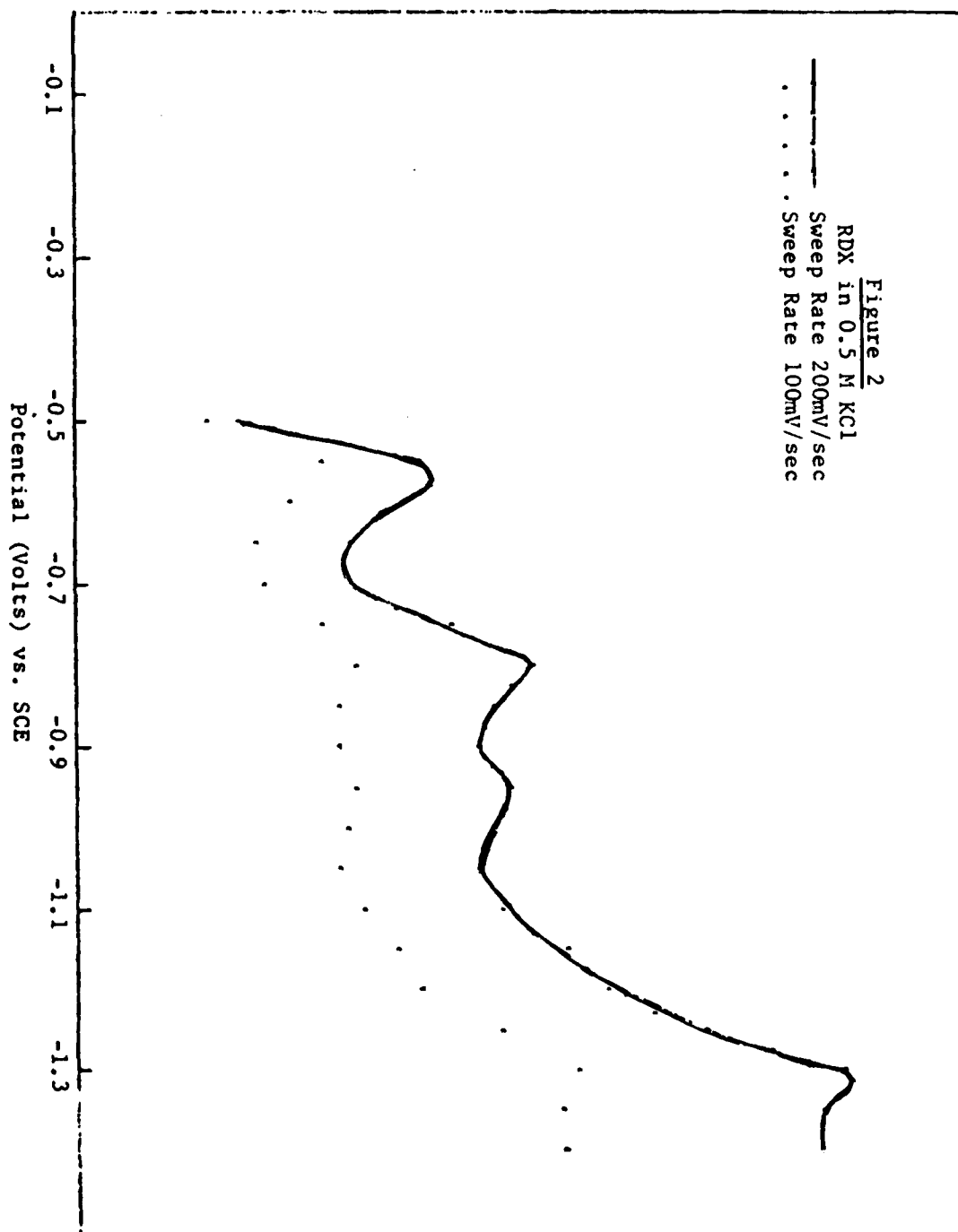
Sweep Rates

Since the solutions studied were not being stirred, diffusion away from or to the electrode governs any mass transport that may take place. Obviously, the nature and the amount of various species available at the electrode for reduction is a direct consequence and, as the rate of sweeping is varied, some difference is expected in the measured quantities. Figure 2 shows the effect of change in sweep rate for polarographs of the same solution of RDX in KCl. The amplitude of the waves are different, but it should be noted that the peak potentials are essentially the same. Thus, it is shown that within the range of sweep rates attempted, the actual sweep rate is unimportant as long as any calibration of current vs. concentration be considered at the same sweep rate.

Peak Potentials for RDX and HMX

Figures 3 and 4 display the reduction waves for HMX and RDX in 0.5 M KCl. It is noted that HMX has a peak at -0.65 volts and a smaller shoulder at -0.95 volts. RDX on the other hand has peaks at -0.58, -0.79, -0.95, and -1.17 volts. Figure 5 shows the waves drawn on the same axis for purposes of comparison. It is seen that HMX and RDX have different Peak Potential Reduction characteristics, but care must be taken in interpretation of these data since one may hide the other. Furthermore, some HMX may often be found in RDX since RDX is prepared from HMX.

Current 10 μ A Full Scale



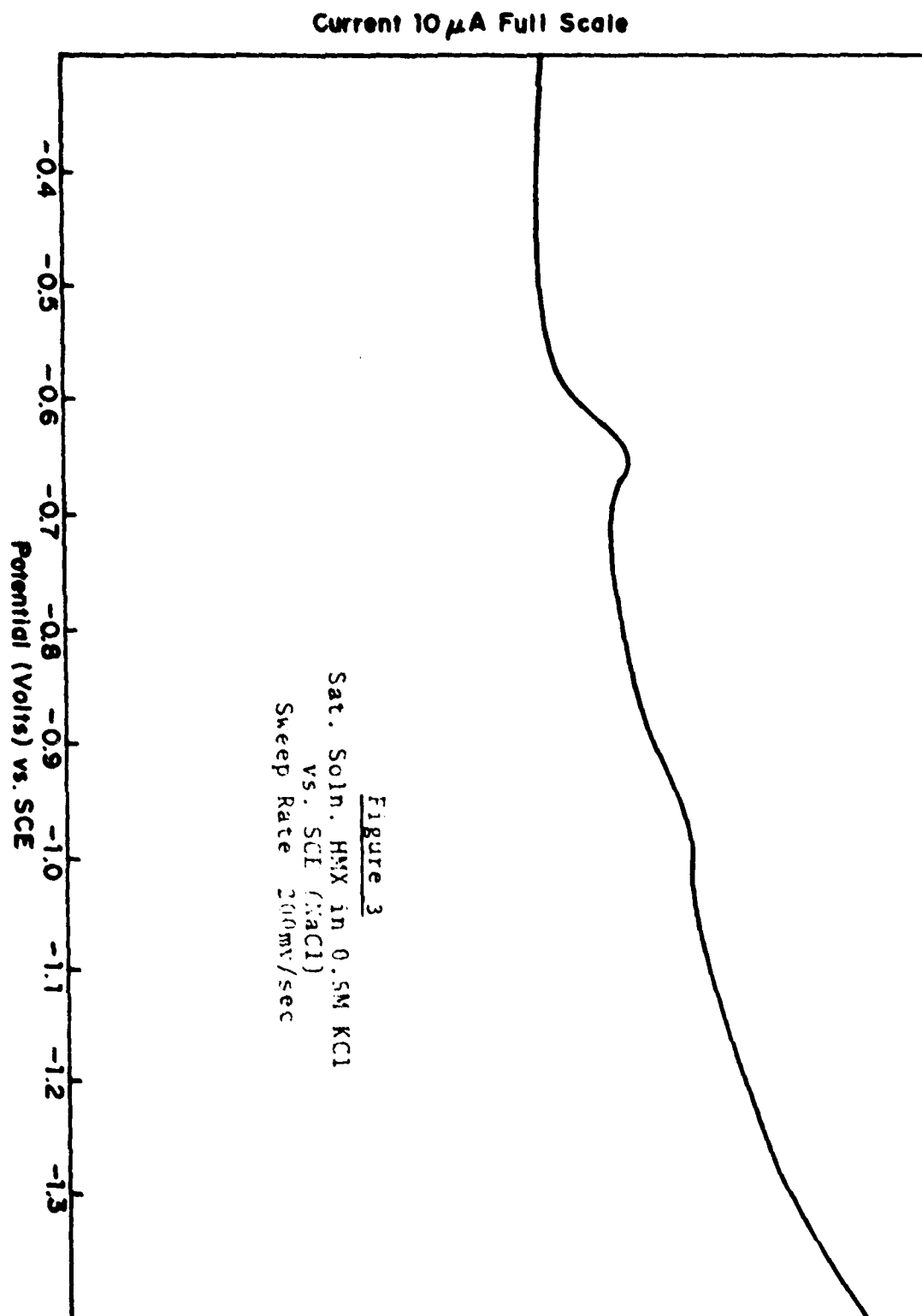


Figure 3
Sat. Soln. H₂X in 0.5M KCl
vs. SCE (NaCl)
Sweep Rate 200mV/sec

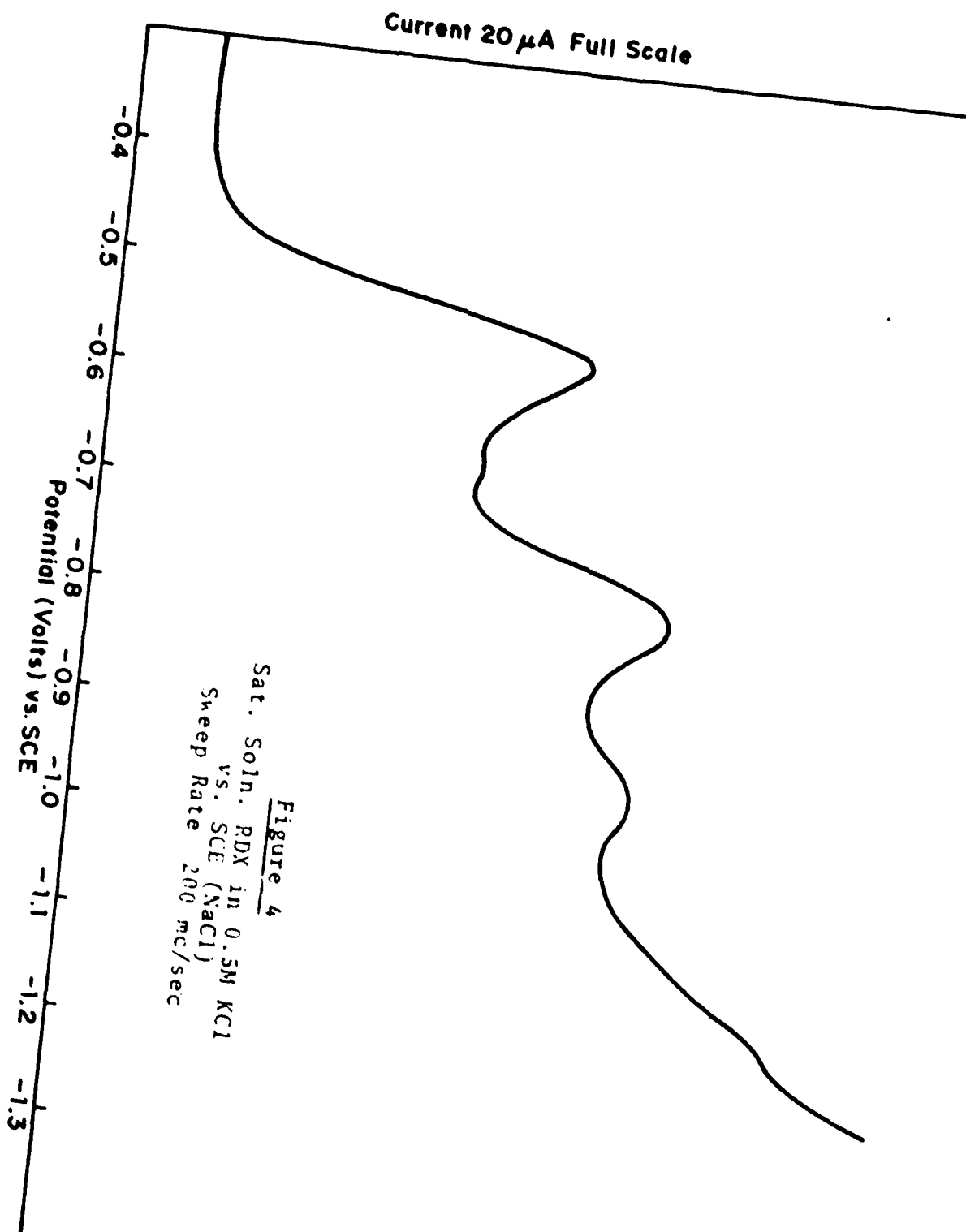
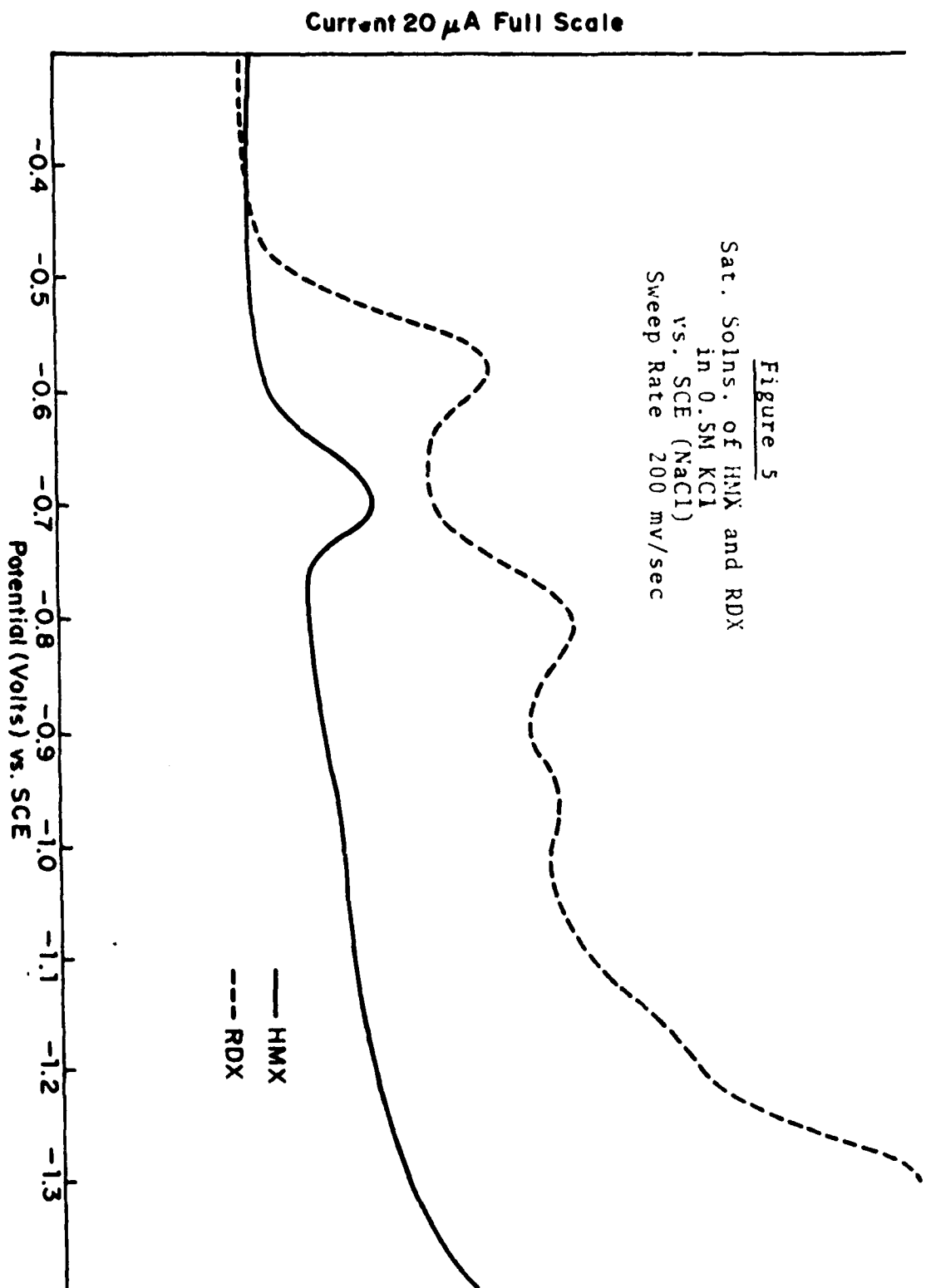


Figure 4
Sat. Soln. RDX in 0.5M KCl
vs. SCE (NaCl)
Sweep Rate 200 mV/sec

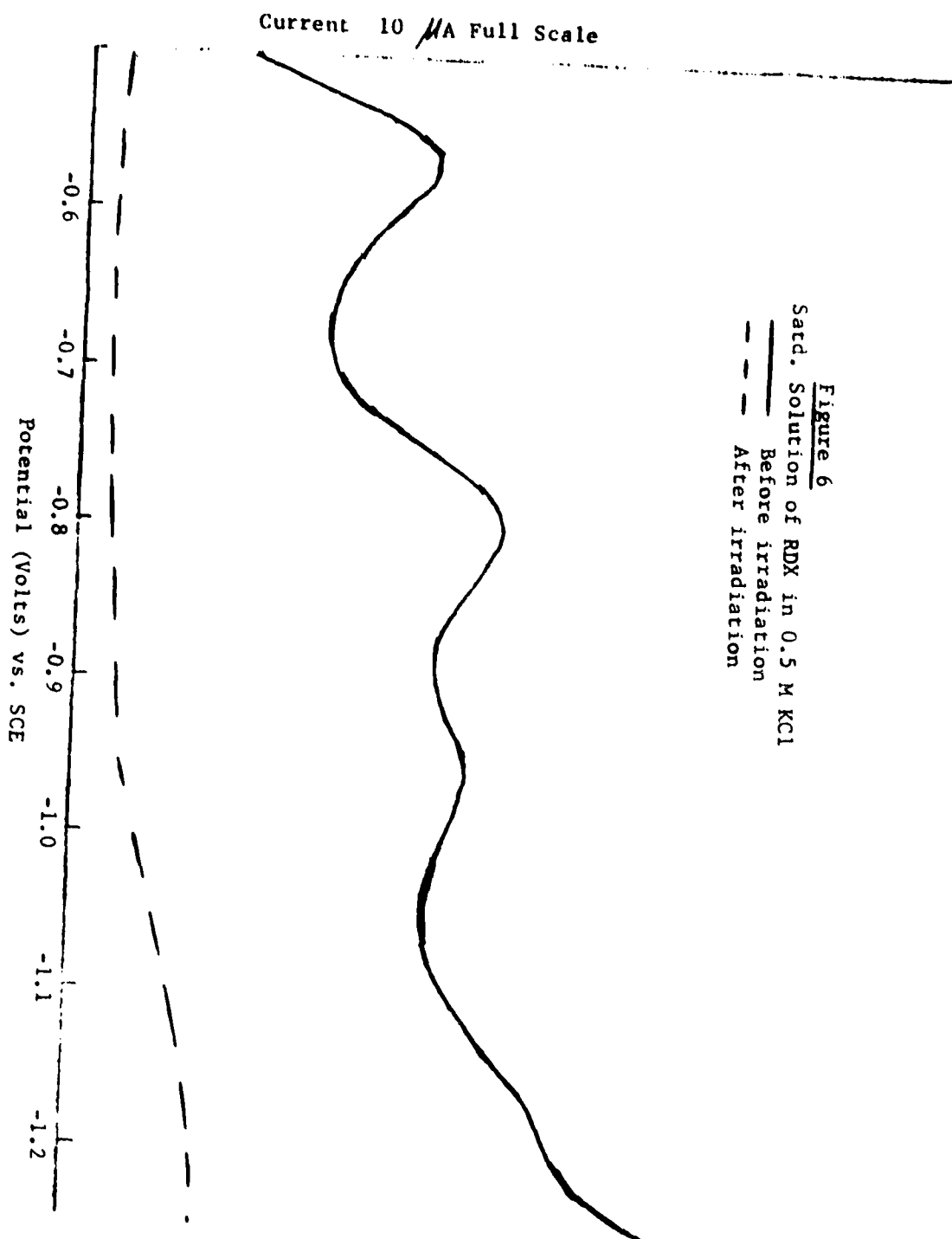


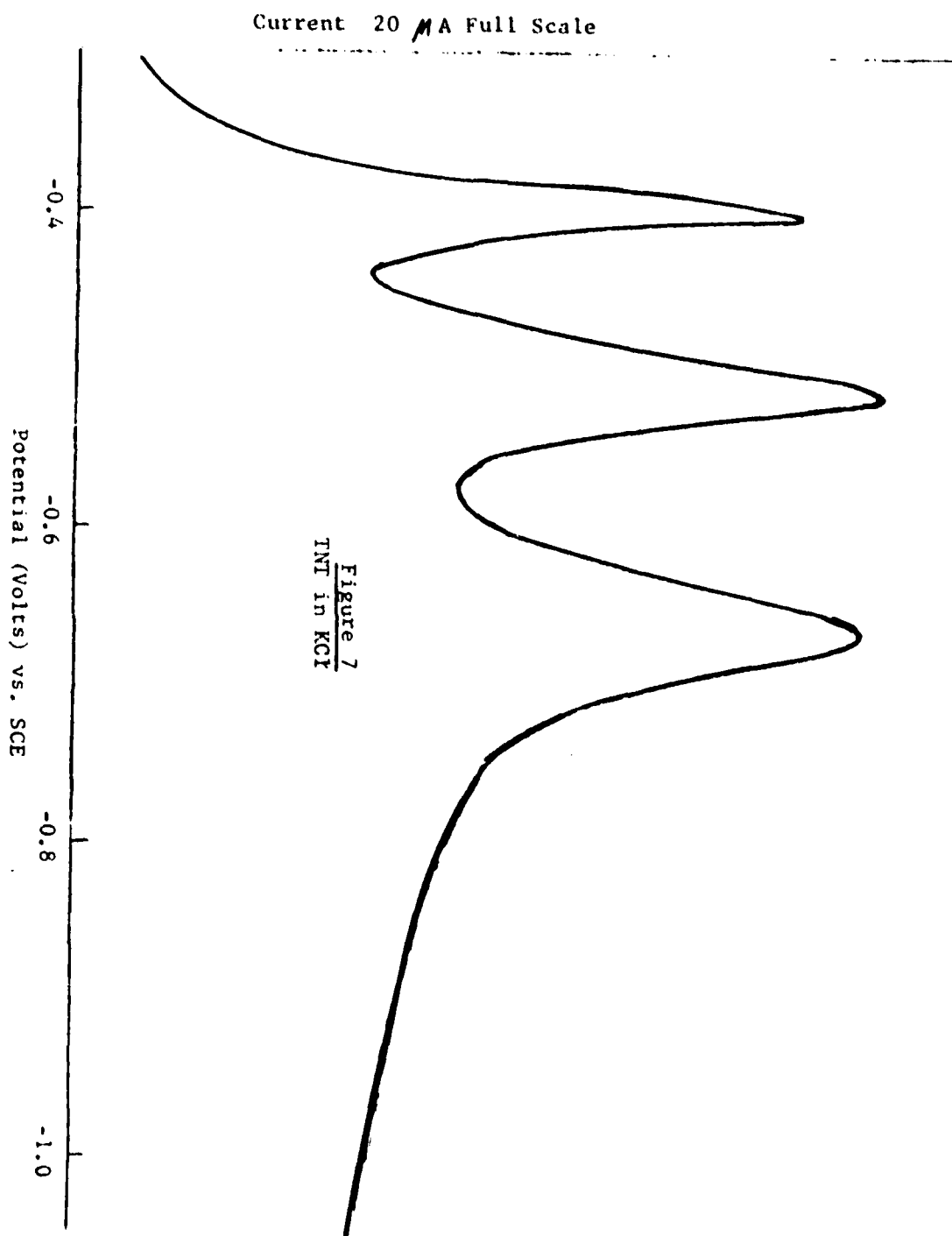
Sample Application

Since it is known that some degradation of organic compounds takes place when exposed to UV light and in an attempt to see differences in concentration of RDX in solution, a preliminary experiment was conducted in which an RDX solution was irradiated with UV light and polarographs obtained both before and after irradiation. Figure 6 displays the polarograms obtained using a saturated solution of RDX in 0.5 M KCl both before and after UV irradiation for 15 minutes. There is no question that degradation of the electrode active species has taken place during this period. The nature of the degradation and the products thereof were not identified. This experiment was repeated in acetate buffer with practically identical results.

Misc.

Single qualitative determinations of TNT and Otto Fuel in KCl were made. Concentrations were not determined so that only the shapes of the resulting curves are of interest (see Figures 7 and 8).





Current 100 μ A Full Scale

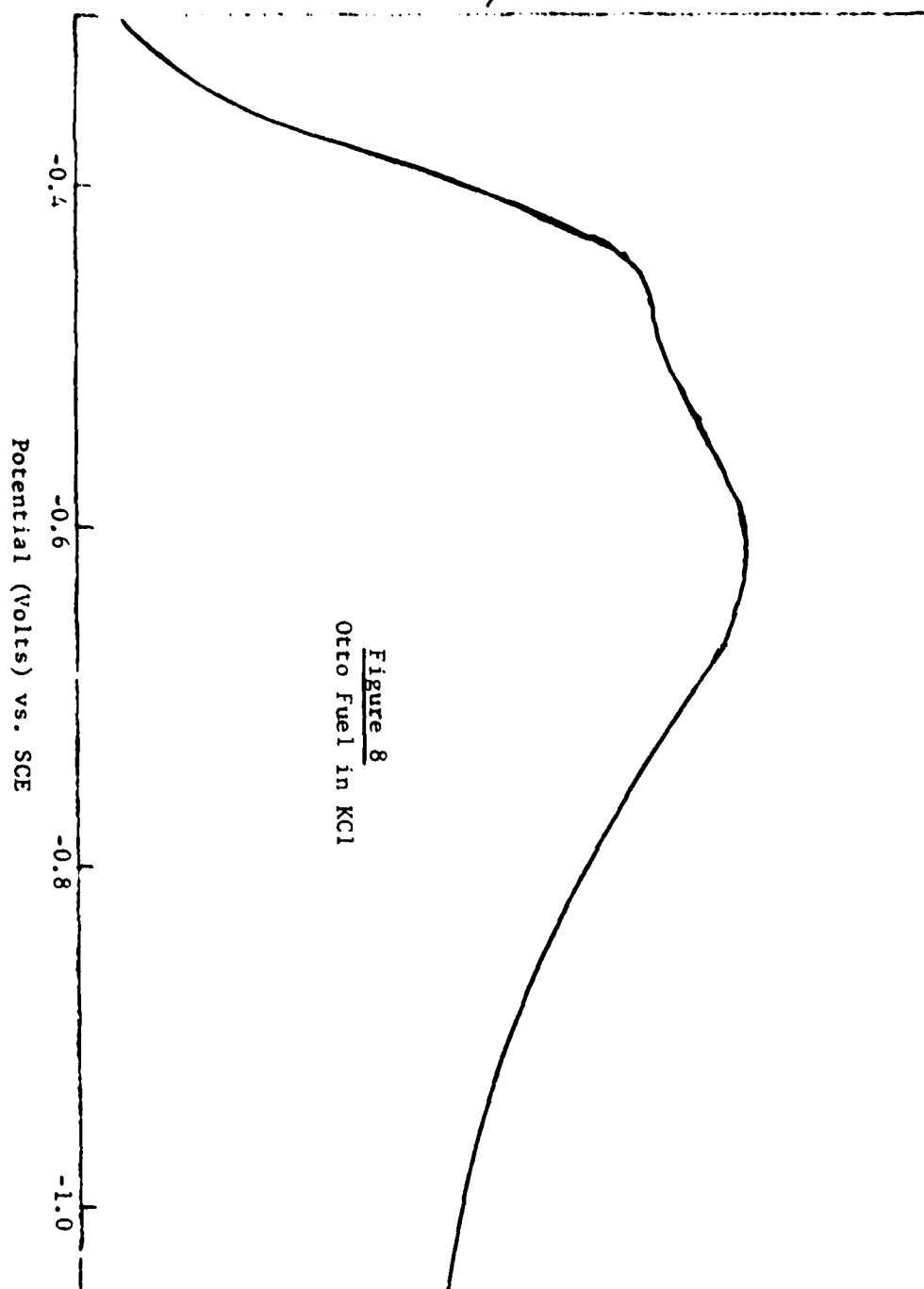


Figure 8
Otto Fuel in KCl

RECOMMENDATIONS

The accumulated data on polarography of ordnance compounds, especially RDX, HMX, TNT, and Otto Fuel indicate that this technique is capable of individual identification of these types of compounds when present in low concentrations in water solutions. No work has been done in this study on solutions of mixed materials to determine the extent to which one compound masks another. Additional work is necessary in order to determine the optimum conditions for analysis of any one compound in a given waste stream. To avoid duplication of effort, it was decided that this study would not be continued. A related investigation is reported by Whitnack.⁷

⁷Whitnack, Gerald C. and Walter J. Becktel, NWC TP 5860 Part 1 of June 1976. "Applied Polarography or Analysis of Ordnance Materials."

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